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BURNING RATE CONTROL FACTORS

IN SOLID PROPELLANTS

Sixth Quarterly Technical Summary Report

For the Period 1 April 1960 to 30 June 1960

Aeronautical Engineering Report No. 446-f

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I. INTRODUCTION

During the past quarter studies of oxidizer particle size effects on burning rate have continued. Methods of oxidizer preparation, propellant preparation and burning rate measurement were described in the Fifth Quarterly Technical Summary Report (Report No. 446e). Experimental results from unimodal and bimodal particle size distributions in a polysulfide binder are reported below. In addition, preliminary results with other fuel types are also reported. The results of this work are rather illuminating with respect to the nature of composite propellant combustion. Some of the results, particularly the appearance of plateau burning, were surprising. Explanations of the behavior observed are being formulated, but are not complete enough to be reported at this time. Analyses of the results will be contained in future reports.

Also during this quarter, a new strand burning apparatus has been completed. This apparatus contains all the features of the chimney strand burner described in the last report, and, in addition, provides controlled temperature of the burning rate vessel and the inlet purge gas. Burning rate measurements have been conducted at temperatures from minus 100 to 200 degrees Fahrenheit, and operation at considerably higher temperatures is possible. Results of this work are described below.

In addition, feasibility studies have been made on methods of measuring the response of burning rate to pressure variations. Experimentation on this subject is contemplated but has not been initiated as yet.

Construction of the Solid Propellant Processing Building is continuing. Details of this facility are contained in Report No. 446a. It is expected that completion of the building and transfer of operations to that site will be completed during the current quarter.

II. EFFECTS OF OXIDIZER PARTICLE SIZE ON BURNING RATES

A. Unimodal Size Distributions

A series of propellants have been formulated incorporating unimodal particle size distributions. The propellant formulation is as follows:

Component		Weight Percent
LP-3	(Thiokol)	32.6
GMF		2.2
Sulfur	(Flowers)	0.2
Ammonium Perchlorate		65.0

This formulation has been temporarily designated LP-3-65 until a systematic propellant designation system is devised.

Oxidizer was prepared in eleven size ranges with mean diameters spaced geometrically from 8 to 265 microns. Each range was of such extent that nominally the ratio of the largest particle diameter to the smallest was 1.4. This system provided size fractions of particles which were geometrically similar, but varying in mean size. Actual size distributions are shown in Figure 1. Particle size distributions were measured by liquid sedimentation as described in Report No. 446d. These fractions were prepared from ground and unground ammonium perchlorate by sieving and air elutriation.

Strand burning rates of these propellants were measured at pressures from 15 to 1600 psia. Results of these measurements are shown in Figure 2. The results are marked by a strong variation of burning rate with particle size at low and intermediate pressures, and a sharp reduction in particle size effect at pressures above 400 psia. The transition from strong to weak size effects is marked by regions of low pressure index or so-called plateau or mesa regions in propellants with the finest oxidizer particles. Data points are shown in only three of the burning rate-pressure curves in order to reduce congestion in the figure.

In order to observe the influence of the width of the particle size distribution on burning rate, two propellants were made using the LP-3-65 formula with broad size distributions. These distributions are shown in Figure 3. The finer size had a mean diameter of 22 microns and was prepared by grinding one time by hammer mill at high hammer speed and high feed rate. The courser material had a mean diameter of 195 microns and was in the condition as received from the manufacturer.

The burning rates of these propellants are shown in Figure 4. Their behavior is found to be similar to those with narrow size distributions and equal mean particle diameters. However, with the finer propellant, the burning rate-pressure index is less in the low pressure region and the plateau region, though clearly observable, is less pronounced. At the high pressure end, burning rates of both propellants are less than those with narrow size distributions. Burning rates of propellants with narrow size distributions and similar mean particle diameters are shown in dashed lines.

It appeared possible that the plateau or transition behavior observed with fine oxidizer might have been an effect produced by the use of strands and might not be representative of motor operation. Thus, a number of motor tests were planned using the LP-3-65 formulation with fine oxidizer. The broad size distribution was used since the narrow distributions produce a mixture the viscosity of which is too great for casting into a motor casing. Two grains were prepared each containing approximately 1600 grams of propellant. The motor used was the same as that used in the acoustic stirring experiments described in Report No. 446a. The grains were case bonded and had cylindrical internal-burning configuration. The port diameter was one-inch and web thickness nearly two-inches. This shape was designed to provide a wide pressure range during the firing in order to cover the entire plateau region during the firing. The burning rates determined from the pressure-time records of the motor firings are also shown in Figure 4. The initial pressure was predicted to be 100 psia. One grain apparently ignited normally, the initial pressure being 80 psia. However, a more energetic igniter was used with the other grain resulting in a high starting pressure and a period of non-equilibrium conditions in the motor chamber.

The results of the motor tests clearly show behavior similar to that of the strands. A low index region is observed between 250 and 500 psia and the burning rates are comparable. From these results it has been deduced that the behavior observed with strand burning in this program is generally similar to what might be expected in motors.

In order to compare the behavior of polysulfide propellants with that of other fuel types, a number of propellants have been prepared with different binders using narrow oxidizer particle size fractions. A series of fine propellants were made using a polyester-styrene copolymer manufactured by the Rohm and Haas Company. This binder was selected since it has been used considerably in this laboratory and a large amount of burning rate data has already been collected with it. The propellant formulation was as follows:

Component	Weight Percent
P-13 (Rohm & Haas)	24.7
Dibutyl Phthalate	2.5
Lecithin	0.15
Nuodex Cobalt	0.10
Methyl Ethyl Ketone Peroxide	0.05
Ammonium Perchlorate	72.5

The temporary designation of this propellant is P-13-72.5A. The small percentage of dibutyl phthalate acts as a plasticizer and allows the cured propellant to be cut into strands with a knife. The fuel content was selected so as to give the same volumetric oxidizer-fuel ratio as with the polysulfide propellants. Thus the propellants would be geometrically similar and the viscosity of the uncured mixture would be low enough for casting. Fine oxidizer for use with this binder was prepared by grinding. It was found that by passing the oxidizer through the grinder several times, a narrow particle size distribution can be obtained. By varying the hammer speed, the mean particle diameter can be varied. Size distributions obtained in this manner are not as narrow as those obtained by elutriation, but the time required for production is much less. The coarse fractions were obtained by sieving. Particle size distributions used are shown in Figure 5.

Burning rate-pressure data obtained with these propellants are shown in Figure 6. The behavior indicated is similar to that of the polysulfide propellants, but there are significant differences. At low pressures, there is a strong inverse relation between burning rate and particle size. However, at high pressures, the fine particle propellants fail to burn where the polysulfide propellants produced plateau behavior. The course particle propellants burn continuously through the high pressure region, but the particle size effects continue to be strong. Thus, there appears to be a strong influence of fuel type on combustion behavior, particularly at high pressures.

In past work by other investigators at Princeton, this binder has been used with higher oxidizer loading. Reid, using an oxidizer loading of 75 percent, found combustion limits similar to those found here with the fine particle polyester-styrene propellant (1). His particle size distribution was probably broad with a mean particle diameter of approximately 25 microns. This conclusion is based on his records of oxidizer grinding procedure. An interesting effect noted by Reid is the broadening of the pressure range over which the propellant burns through the use of wider strands. This result indicates that these propellants might burn throughout the pressure range if used in a motor. Thus, the desirability of a motor test is apparent to see if plateau behavior occurs in this region.

Taback, using an oxidizer loading of 77.5 percent, found no evidence of combustion limits or plateau behavior (2). These results indicate that these unusual behavior patterns may be typical only of very fuel-rich propellants.

A third fuel-binder has been used in order to continue investigation of the effects of binder variation. This binder is Epon 812, an epoxy resin manufactured by the Shell Chemical Company. This binder differs from the others used in that it has a higher oxygen content. Thus, with the same weight fraction, a more nearly stoichiometric mixture is obtained. The formula used with this binder is as follows:

Component	Weight Percent
Epon 812 (Shell)	29.0
Dibutyl Phthalate	3.2
Triethylene Tetramine	0.3
Ammonium Perchlorate	67.5

Again the dibutyl phthalate is employed as a plasticizer, and the fuel concentration was selected to provide similar volumetric loading as used in previous propellants.

Only one propellant batch has been prepared as yet using this formula. Oxidizer was prepared in a narrow size distribution by multiple grinding with a resulting mean particle diameter of 10 microns. Burning rates obtained with this propellant are shown in Figure 7. As indicated, this fine particle propellant burns throughout the pressure range with a rather high burning rate-pressure index and no combustion limits or plateau behavior. It is planned to continue the investigation with this binder using lower oxidizer contents in order to see if plateau behavior appears.

B. Bimodal Size Distributions

Most propellant formulations currently in use incorporate blends of oxidizer of widely different particle sizes. This is usually accomplished by using a mixture of unground and finely ground oxidizer. Such bimodal size distributions allow much higher oxidizer concentration than is practical with unimodal distributions. Thus, it is of interest to study particle size effects in this type of propellant.

A series of fine propellants was prepared using the LP-3-65 formulation, 30 percent of the oxidizer being a narrow size fraction of small diameter particles, and 70 percent being a narrow fraction of coarse particles. Mean particle diameters of both the coarse and fine fractions were varied in order to observe oxidizer particle size effects. Burning rate-pressure data for these propellants are shown in Figure 8. For comparison, burning rate curves of two propellants with unimodal distributions are shown in dashed lines.

Among the five propellants there appears to be only a mild effect of oxidizer particle size variations. Generally, the propellants containing the finest particles have the highest burning rates, but the differences are not great. However, when the bimodal distribution propellants are compared with those containing unimodal distributions, significant differences are apparent. The bimodals as a group at low pressures, burn with rates comparable to those of the unimodals with the finest particles. At high pressures the rates of the bimodals are less than those of all the unimodals. As a result the burning rate-pressure indices of all the bimodals are considerably less than those of the unimodals.

It would appear from these results that when oxidizer particles of widely different sizes are present, that the finer particles determine the burning rate at low pressures, and that at high pressures the partial use of fine particles reduces the rate from what it might be even if all the particles were coarse. These results agree with those obtained with broad unimodal size distributions which were described earlier.

C. Burning Surface Studies

In order to gain a better understanding of the burning process, it was decided that studies of the burning propellant surface should be undertaken. Photography of burning strands has been undertaken at Princeton and in other laboratories, and further efforts are being made along this line. But resolution of the order of particle diameters is difficult to obtain during burning, particularly at high pressures. Thus, it was decided to try a method of extinguishment which would leave the propellant surface intact and allow microscopic studies where burning had taken place. This was accomplished by means of a pressure vessel in which small pieces of propellant could be burned, and which could be evacuated to sub-atmospheric pressures very quickly. The apparatus is shown schematically in Figure 9. A propellant strand is mounted in a six-inch flanged dome. The dome is attached to a rupture disc assembly containing a standard six-inch rupture disc of desired strength. This assembly is then bolted to a matching flange on a large dump tank. The ratio of tank volume to dome volume is approximately 175. To operate, the tank is evacuated to a few millimeters of mercury absolute pressure and the dome is pressurized with nitrogen to a pressure somewhat below the rupture pressure of the disc. The propellant is ignited by means of a hot wire and the combustion products cause the pressure to increase to the rupture pressure. When the disc fails, the pressure drops suddenly and the propellant is extinguished. Samples of many propellants have been extinguished in this way at pressures from 300 to 1000 psi. Continued testing is planned at lower pressures and photomicrographs of propellant surfaces are being made so that they may be compared and presented in future reports.

The results found in these studies thus far are shown schematically in Figure 10. The sketches were drawn from observations of propellant surfaces through a stereoscopic microscope. As indicated, the nature of the burning surface varies strongly with changes in particle size and with pressure changes. At low pressure with small particles, the surface is generally irregular, the roughness being large compared with the particle sizes. With large particles, the surface is flat with oxidizer particles clearly visible and protruding above the fuel surface. At high pressure with small particles, the surface is flat with small irregularities and no particles are visible. With large particles, the surface takes on a worm hole appearance. The oxidizer crystals appear to burn faster than the fuel leaving holes with width and depth comparable to the crystal diameters. Often an extinguished crystal will be found at the bottom of a hole.

These results have been observed with both polysulfide and polyester-styrene propellants.

Results with bimodal particle size distributions are generally combinations of the above results. Fine particle behavior is observed along with the coarse particles.

More complete descriptions of these results, including photographs will follow in future reports.

D. Conclusions

In order to show more clearly the effect of particle size on burning rate, the data for polysulfide propellants with narrow unimodal particle size distributions has been replotted in Figure 11. Here the coordinates are burning rate versus particle size with pressure as a parameter. Four zones of behavior are evident in the figure and these have been outlined by dashed lines.

Zone 1 includes fine particle propellants at low pressures. Here burning rates are insensitive to particle size, but increase strongly with pressure. These characteristics would indicate a process controlled by a gas phase chemical reaction which is slow compared to the diffusional mixing of fuel and oxidizer.

Zone 2 covers coarse particle propellants at low pressures. Here rates are inversely related to particle size and pressure sensitivity is slightly lower than in zone 1. The particle size dependence and the nature of the burning surfaces indicate a process controlled by both gas phase chemical reaction and diffusional mixing of oxidizer and fuel gases. This behavior is similar to that predicted by the granular diffusion flame theory which includes both these processes.* The data in this region fit this theory rather well, however, the dependence of burning rate on particle size as reflected in the diffusion parameter "b" is less than predicted.

Zone 3 includes coarse particle propellants at high pressures.

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*The granular diffusion flame theory developed by Summerfield and coworkers at Princeton is described in Report No. 446a.

Rates here are insensitive to particle size and only moderately pressure dependent. From these results and the appearance of the burning surface, it is concluded that in this region burning is controlled by ammonium perchlorate decomposition. The perchlorate particles decompose below the fuel surface with pyrolysis and oxidation of the fuel taking place above. There is evidence to show, however, that the process is not a continuous one, but rather an intermittant process. When one oxidizer crystal is consumed, adjacent crystals may still be insulated by a fuel layer which must be removed before perchlorate decomposition can commence. This results in a lower overall burning rate than that at which the crystals are consumed. This would explain why some of these propellants burn more slowly than pure ammonium perchlorate at the same pressures. Ammonium perchlorate burning rates have been published by Friedman (3). Also this would explain the reduced burning rates when broad particle size distributions are used. In these propellants, the fuel layers between particles are thicker and the delay before particle ignition would be longer.

This hypothesis as yet has no quantitative foundation, but is drawn from the evidence which has been presented here. Attempts to check it quantitatively will be made in the future.

Zone 4 is a region of unusual behavior. It includes small particle propellants at high pressures. Some propellants exhibit plateau behavior here, some fail to burn, and others continue burning in a manner similar to that in zone I. No clear explanation can be presented at this time for this variety of phenomena. However, it is believed that this zone does not represent a different behavior pattern, but rather is a region of transition from zone I to zone 3. The manner in which this transition is accomplished varies with different propellants. This zone will receive more study in the future since it would be of interest to gain an understanding of the processes involved.

On the basis of the results obtained thus far in this program, the following qualitative conclusions have been drawn:

1. As particle size and pressure are varied, the nature of the combustion process changes. At least three distinct regions of behavior are evident and each would require a different model for theoretica. treatment.

2. When bimodal particle size distributions are employed, different size particles appear to dominate the combustion process in different pressure ranges. Thus, these propellants have characteristics desirable for propellant applications, but are unsuitable for fundamental studies of combustion behavior. The combining of two different modes of burning adds greatly to the complexity of the process.

This work will continue in the future with more emphasis on the theoretical analysis of the results which have been obtained.

III. EFFECT OF TEMPERATURE ON BURNING RATE

As indicated in previous reports, construction of new strand burning apparatus has been underway. This apparatus was completed and placed in operation during the past quarter. It incorporates the chimney configuration of the strand burner previously used which was described in Report No. 446e. It is this configuration which reduces the necessity of inhibitor coatings and maintains a level burning surface, thereby improving the accuracy of burning rate measurements.

In addition, the new apparatus incorporates means for controlling the temperature of the burner vessel and that of the incoming purge gas. This is accomplished through the use of a heat exchanger in the purge gas line. Both the burner vessel and the heat exchanger are immersed in an insulated constant temperature bath. Low temperature measurements are made using ice-antifreeze mixtures or dry-ice-acetone mixtures. The apparatus has been operated at temperatures down to minus 100°F in this manner. High temperature runs are made through the use of electric immersion heaters and appropriate bath liquids. Measurements have been made at temperatures up to 200°F in water baths, and operation is possible to much higher temperatures using low vapor pressure oils.

In addition to providing variable temperature operation, the new apparatus also maintains a constant temperature for burning rate measurements at room temperatures. This is an improvement over the previous system where no such control was provided.

Initial testing has been conducted with polyester-styreno-ammonium perchlorate propellants. Burning rate-temperature indices have been determined for these propellants over a wide temperature range. In addition, some unusual behavior has been noticed such as variations of combustion limits with temperature. It is expected that this work will continue and that results will be reported in detail in future reports.

IV. BURNING RATE RESPONSE TO PRESSURE VARIATIONS

The rate at which the burning rate of a solid propellant adjusts itself to changes in pressure is a subject of interest to those studying the combustion process. This rate of adjustment may very well have a bearing on such phenomena as combustion instability and other behavior patterns. Experimentation intended to investigate this subject is contemplated and possible methods are being studied. However, effort thus far has not proceeded beyond this point.

REFERENCES

1. Reid, Donald L., "The Dependence of Several Solid Propellant Burning Anomalies on Flame Structure," Report No. 394, Department of Aeronautical Engineering, Princeton University, July, 1957.

2. Taback, Harold J., "The Effects of Several Composition Factors on the Burning Rate of an Ammonium Perchlorate Solid Propellant," Report No. 429, Department of Aeronautical Engineering, Princeton University, September, 1958.

3. Friedman, Raymond; Levy, Joseph B. and Rumbel, Keith E., "The Mechanism of Deflagration of Ammonium Perchlorate," AFSOR-TN 59-173, Atlantic Research Corporation, February, 1959.

LIST OF ILLUSTRATIONS

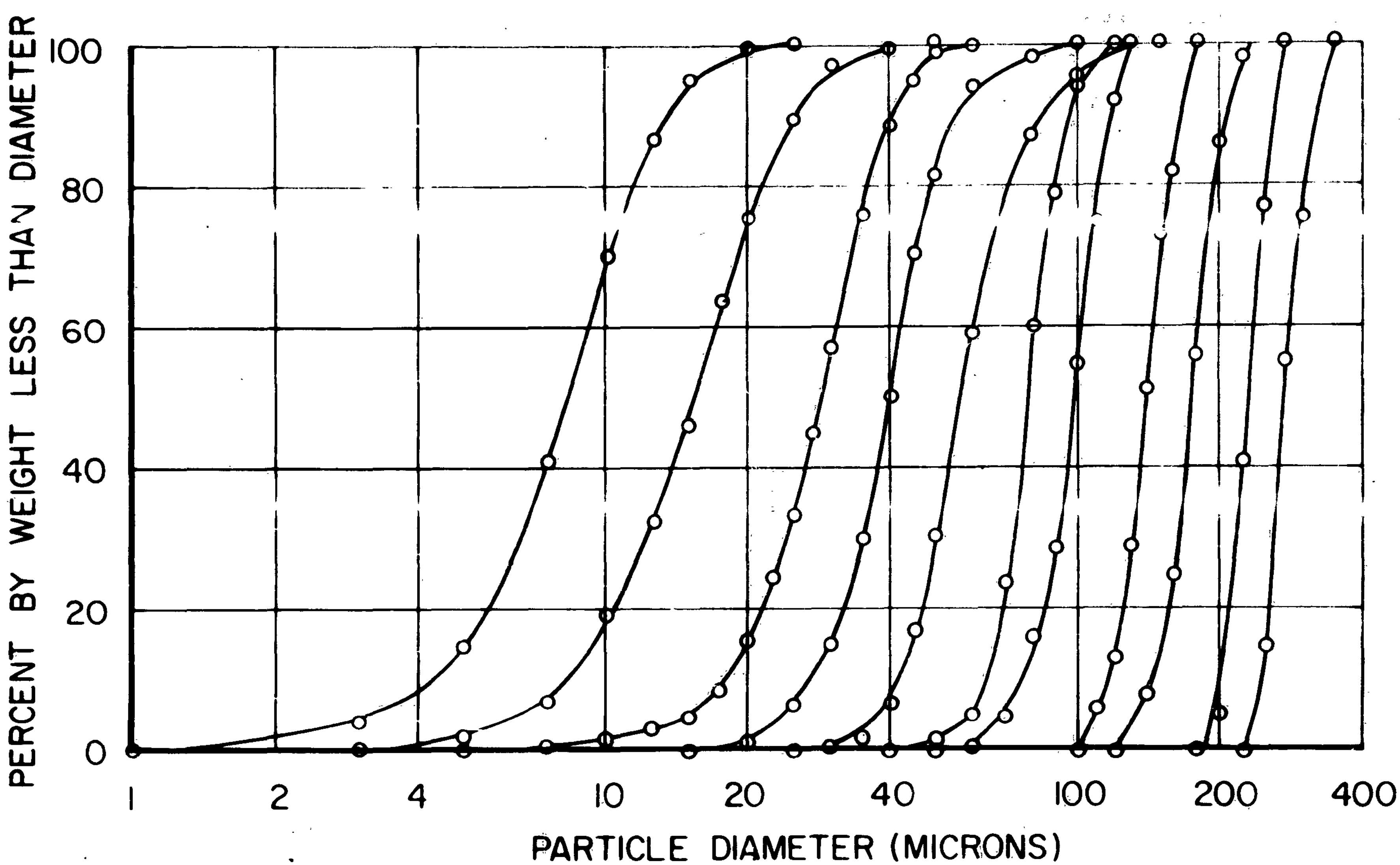

FIGURE I OXIDIZER PARTICLE SIZE DISTRIBUTIONS, NARROW FRACTIONS

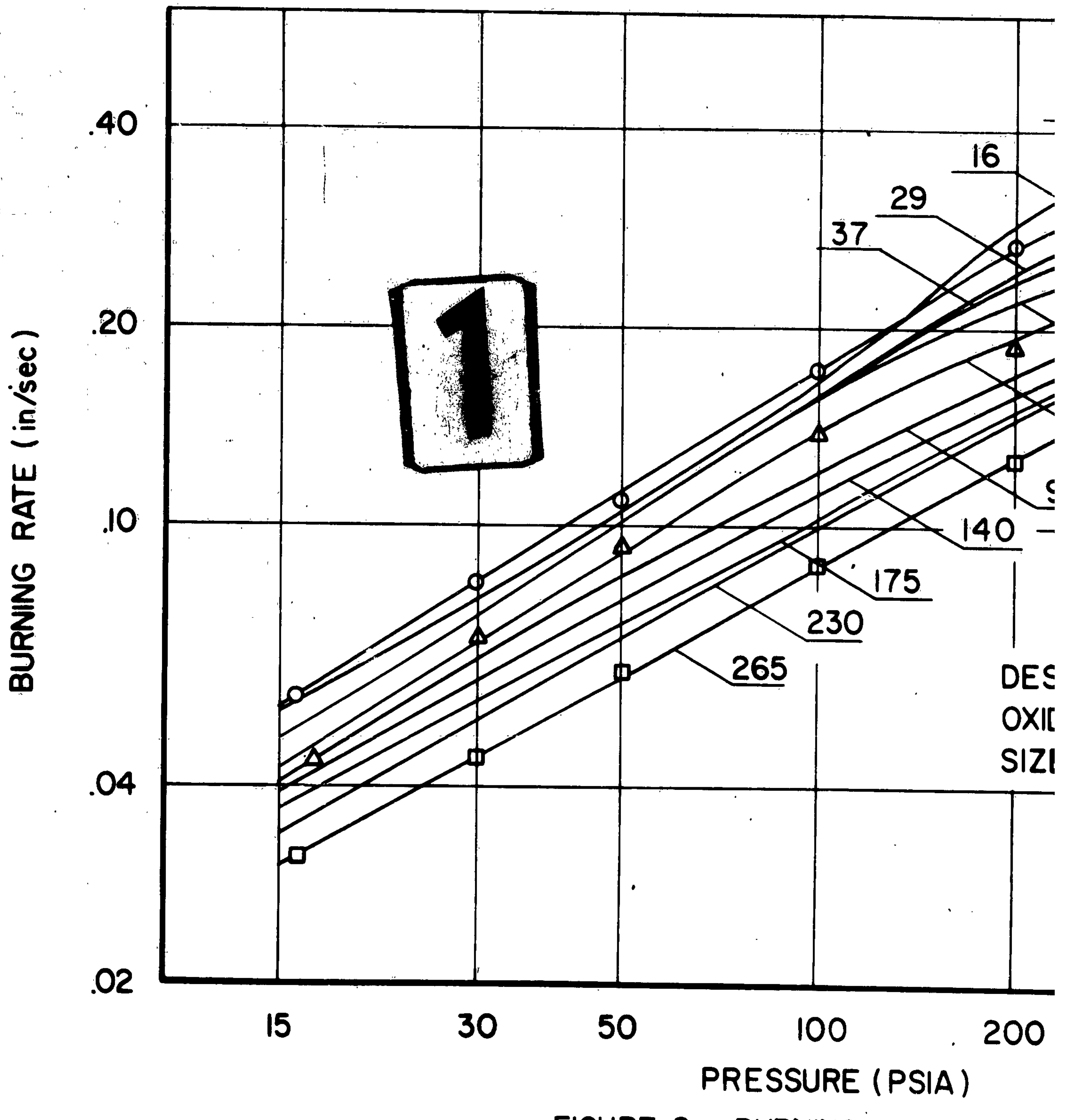

FIGURE 2 BURNING RATE VS P
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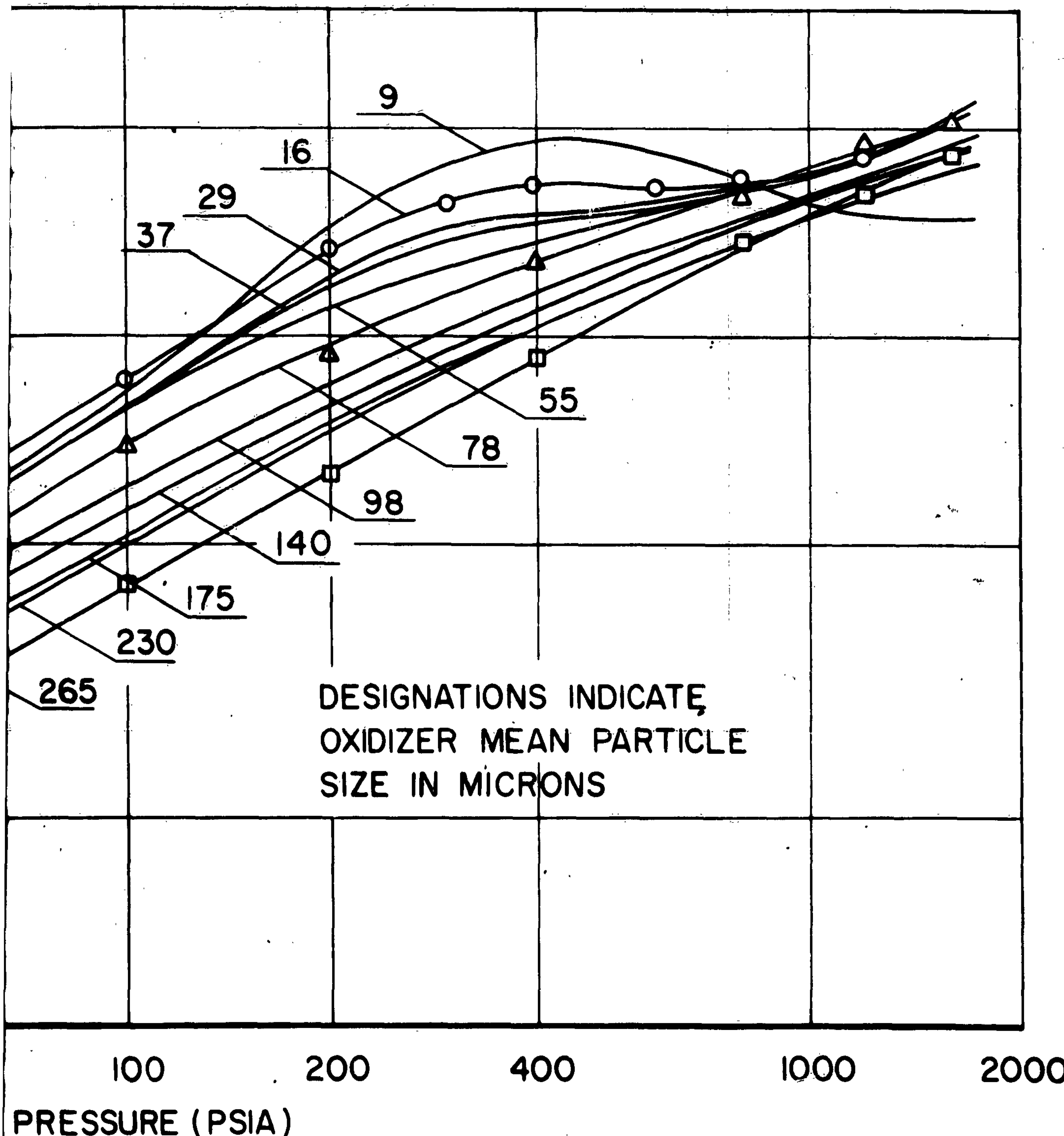
PARTICLE SIZE DISTRIBUTI



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BURNING RATE VS PRESSURE
PROPELLANTS, NARROW UNIMODAL
TICLE SIZE DISTRIBUTIONS

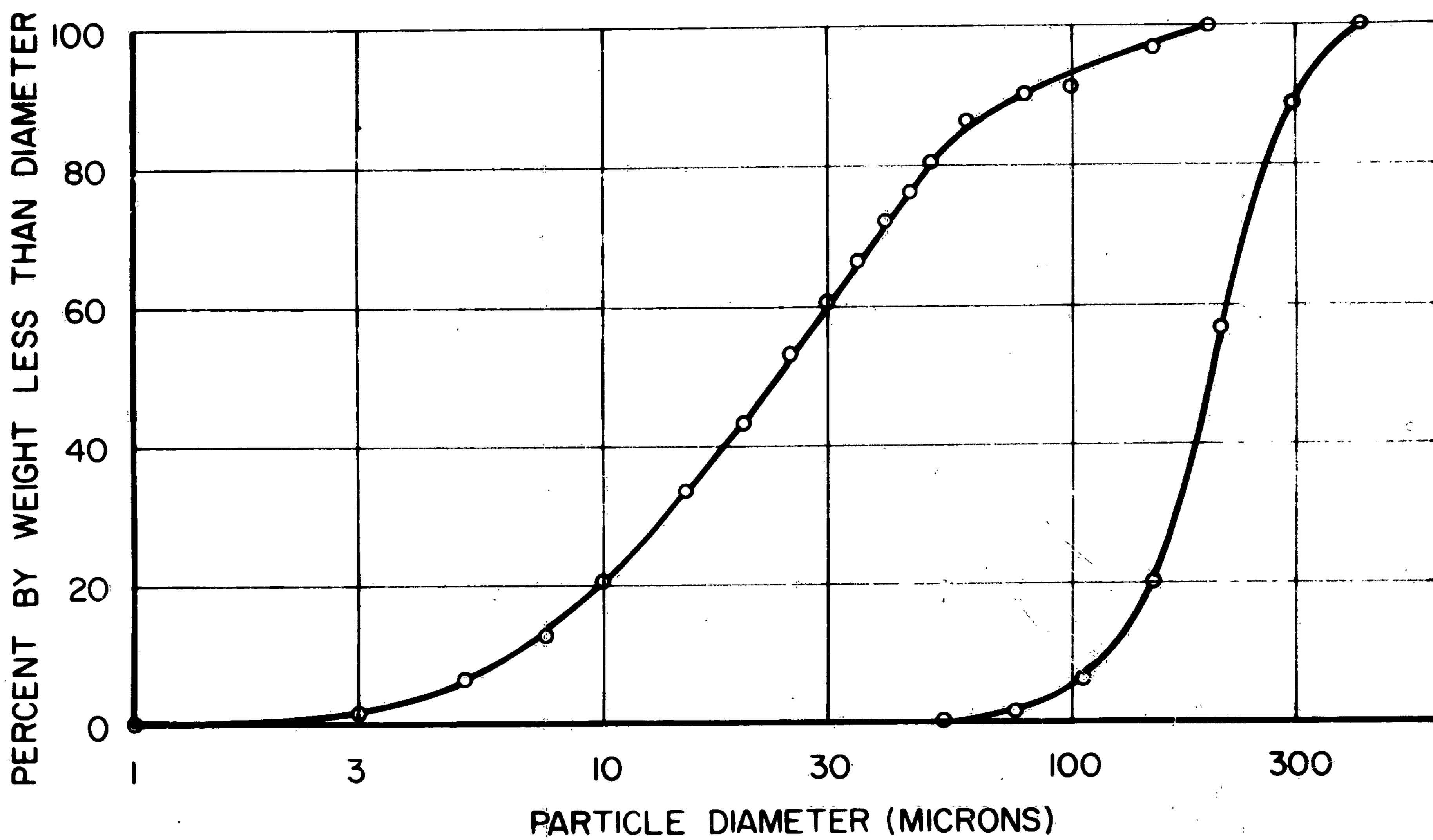


FIGURE 3 OXIDIZER PARTICLE SIZE DISTRIBUTIONS, BROAD FRACTIONS

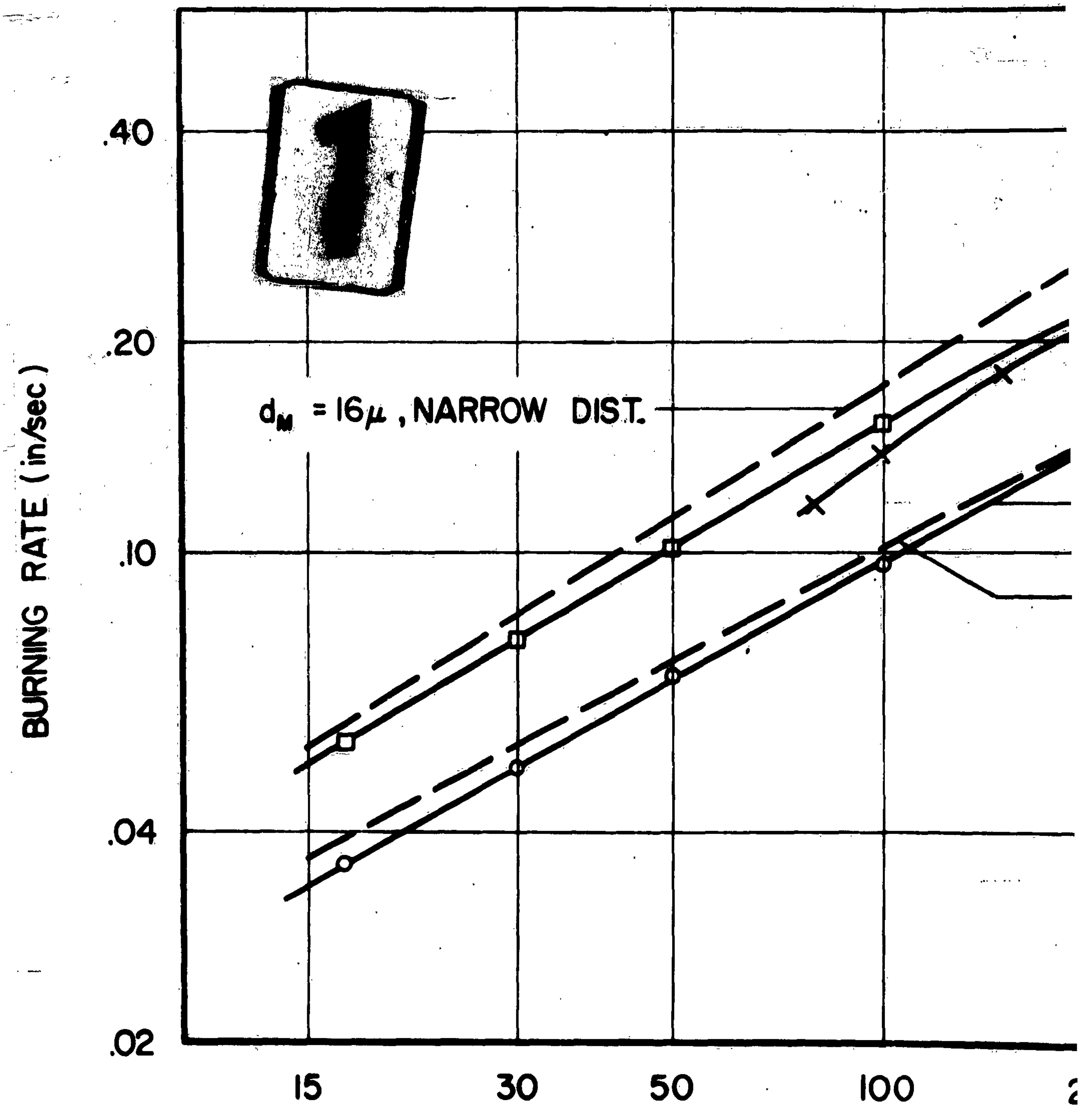
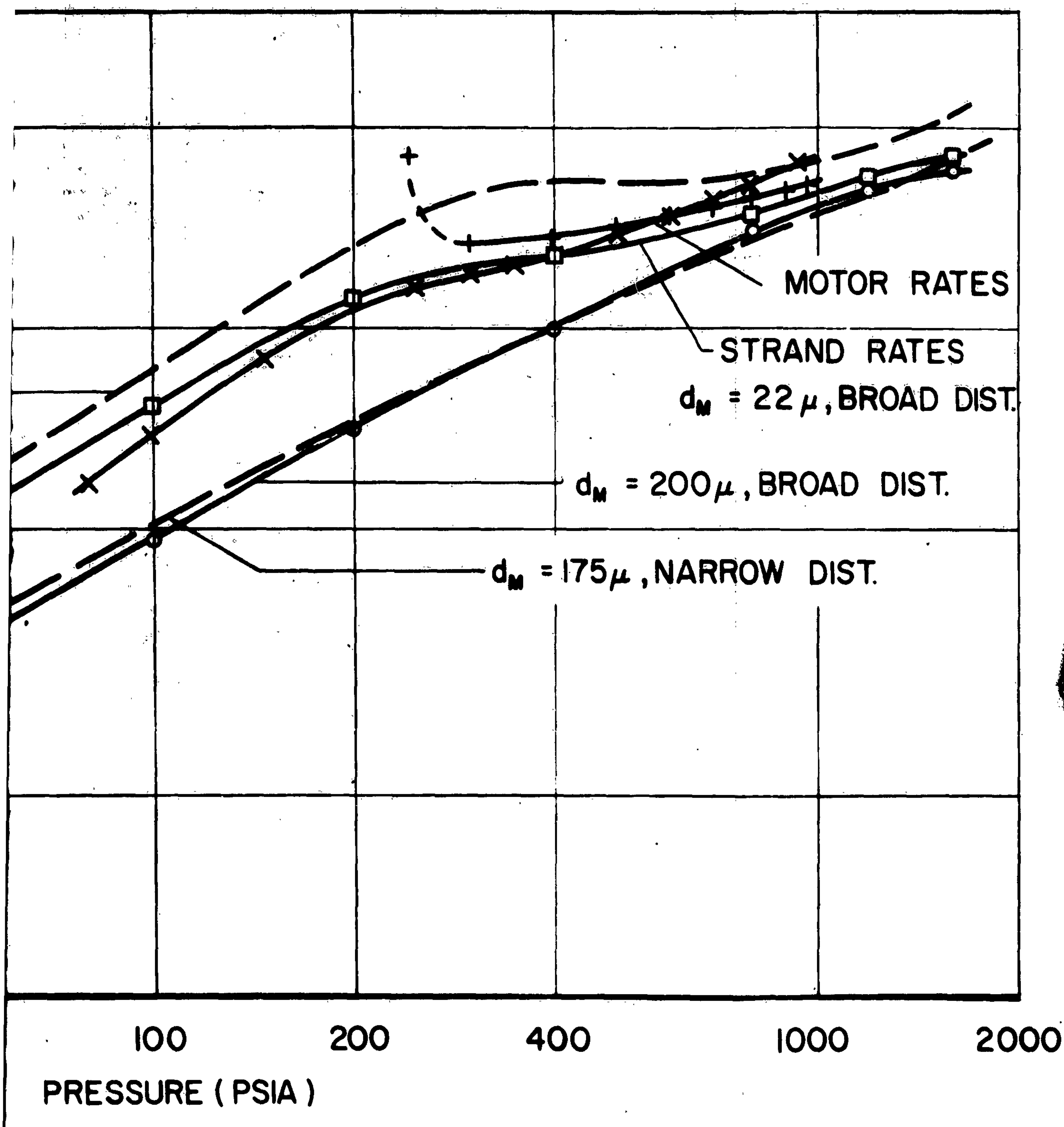


FIGURE 4 BURNING RATE V
POLYSULFIDE PROPELLANTS, B
PARTICLE SIZE DISTRIBUT



4 BURNING RATE VS PRESSURE
DE PROPELLANTS, BROAD UNIMODAL
TICLE SIZE DISTRIBUTIONS

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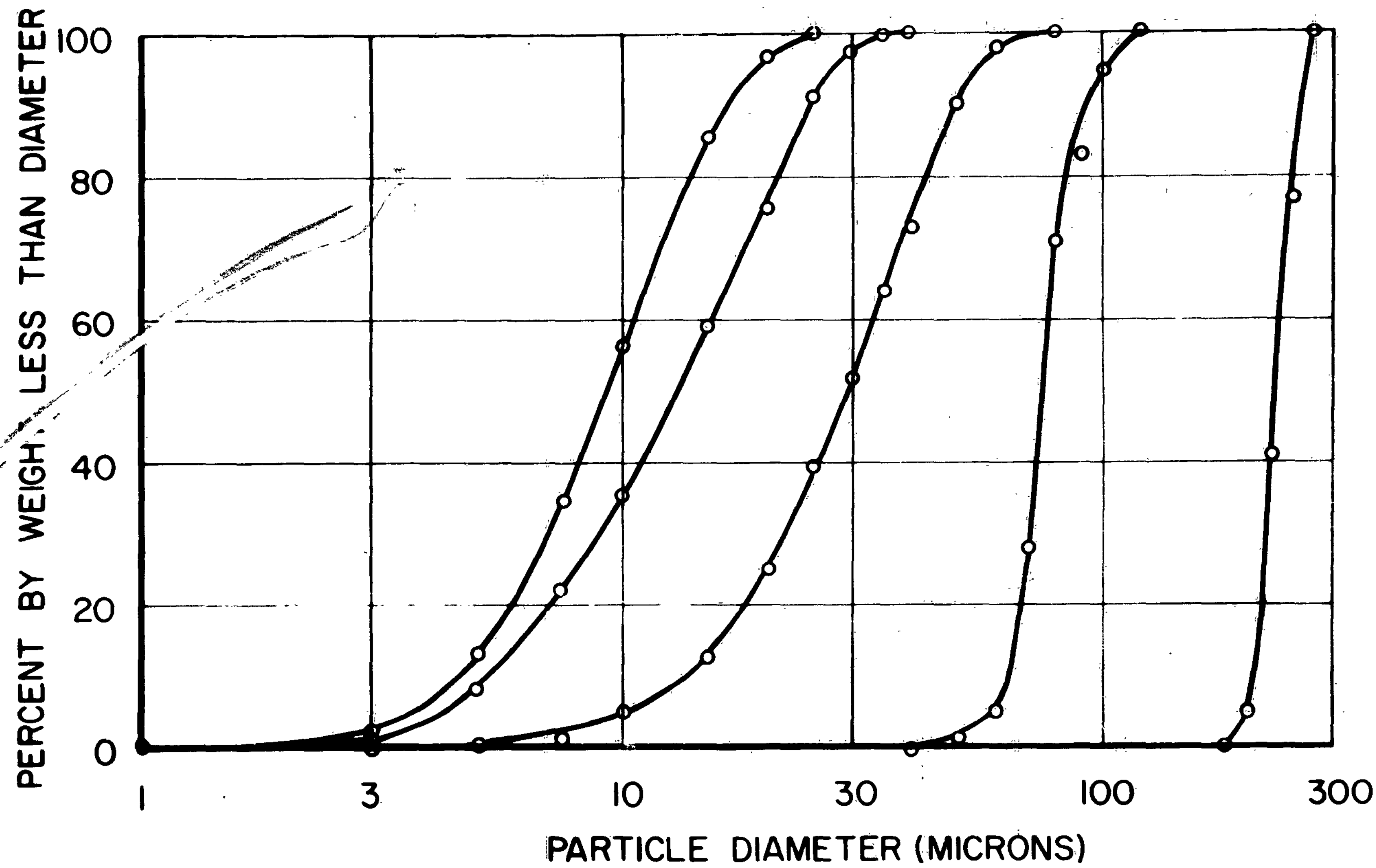

FIGURE 5 OXIDIZER PARTICLE SIZE DISTRIBUTIONS,
NARROW FRACTIONS USED WITH POLYESTER - STYRENE POLYMER

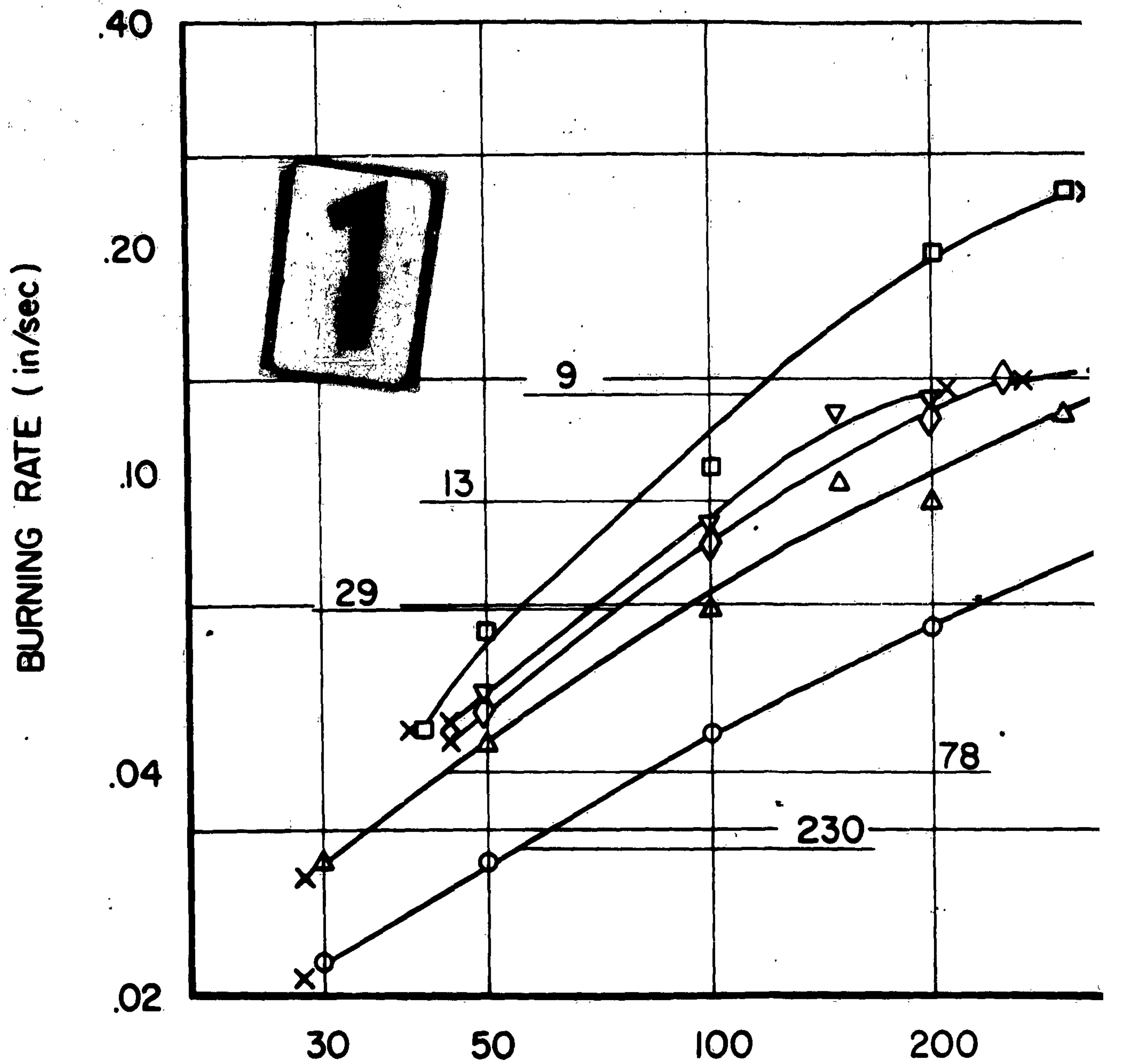

FIGURE 6 BURNING RATE

POLYESTER – STYRENE PROPELLA

PARTICLE SIZE DISTI

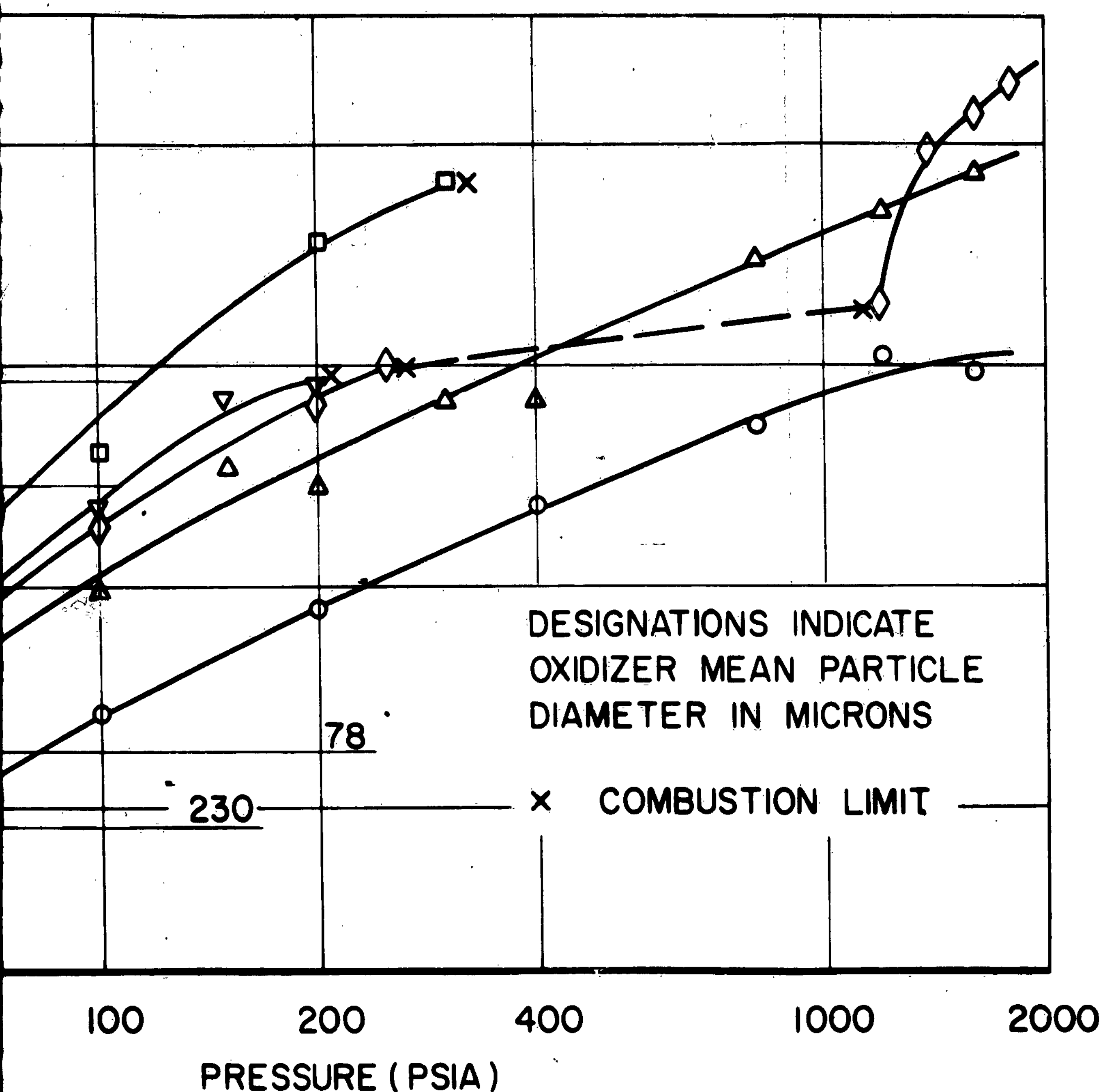

FIGURE 6 BURNING RATE VS PRESSURE
STER - STYRENE PROPELLANTS, NARROW UNIMODAL
PARTICLE SIZE DISTRIBUTIONS

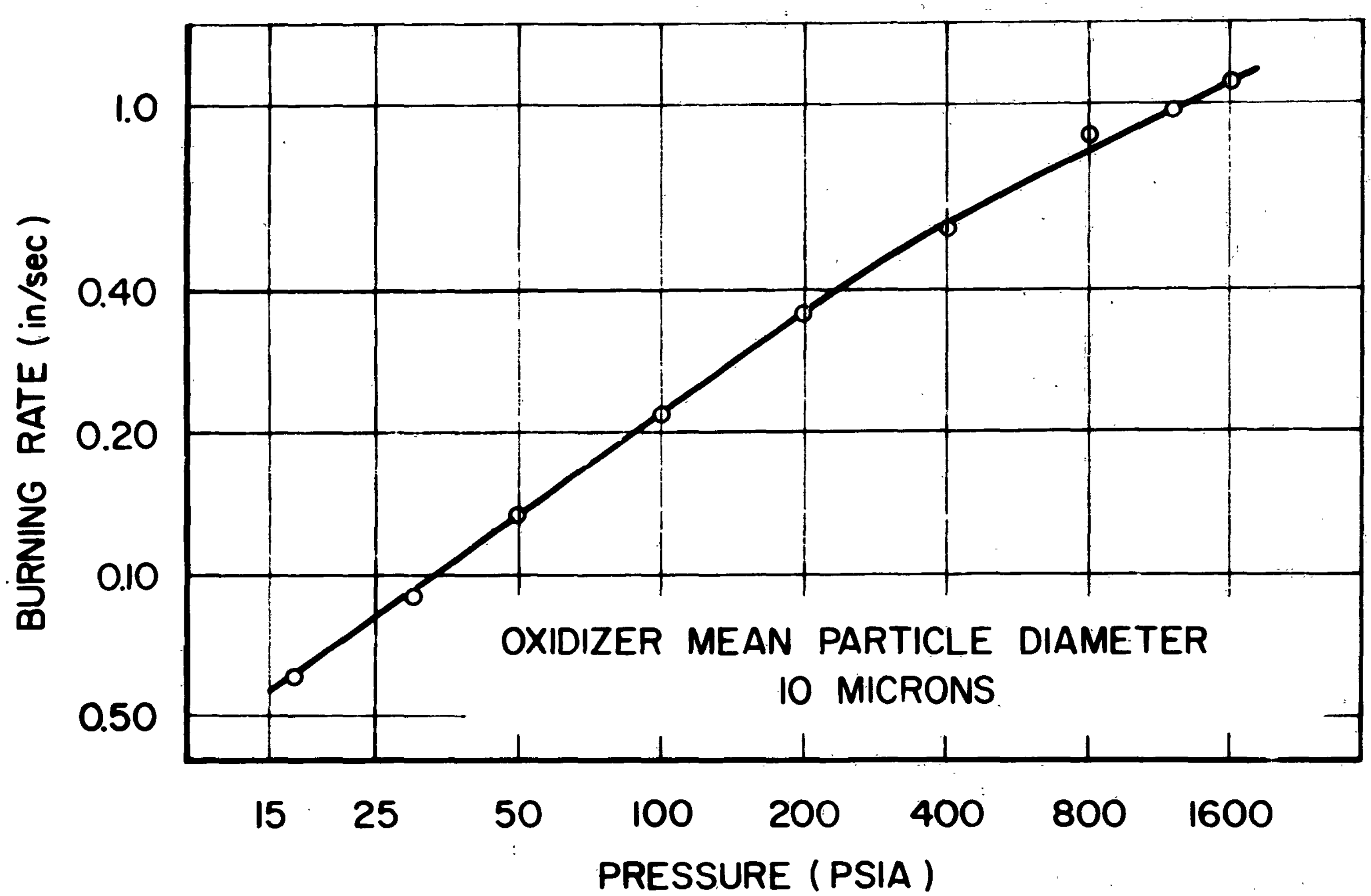

FIGURE 7 BURNING RATE VS PRESSURE
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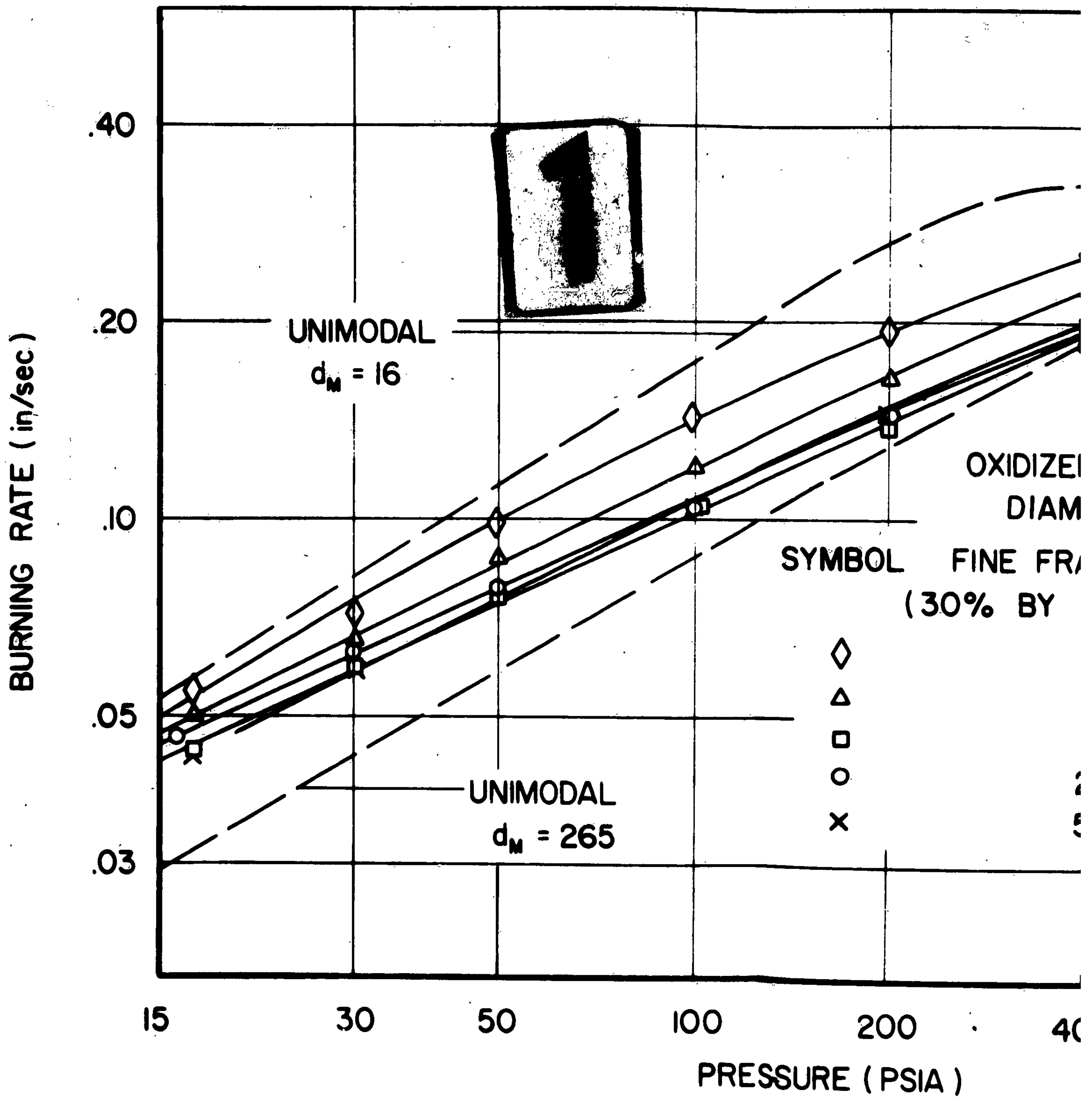

FIGURE 8 BURNING RATE VS PRE
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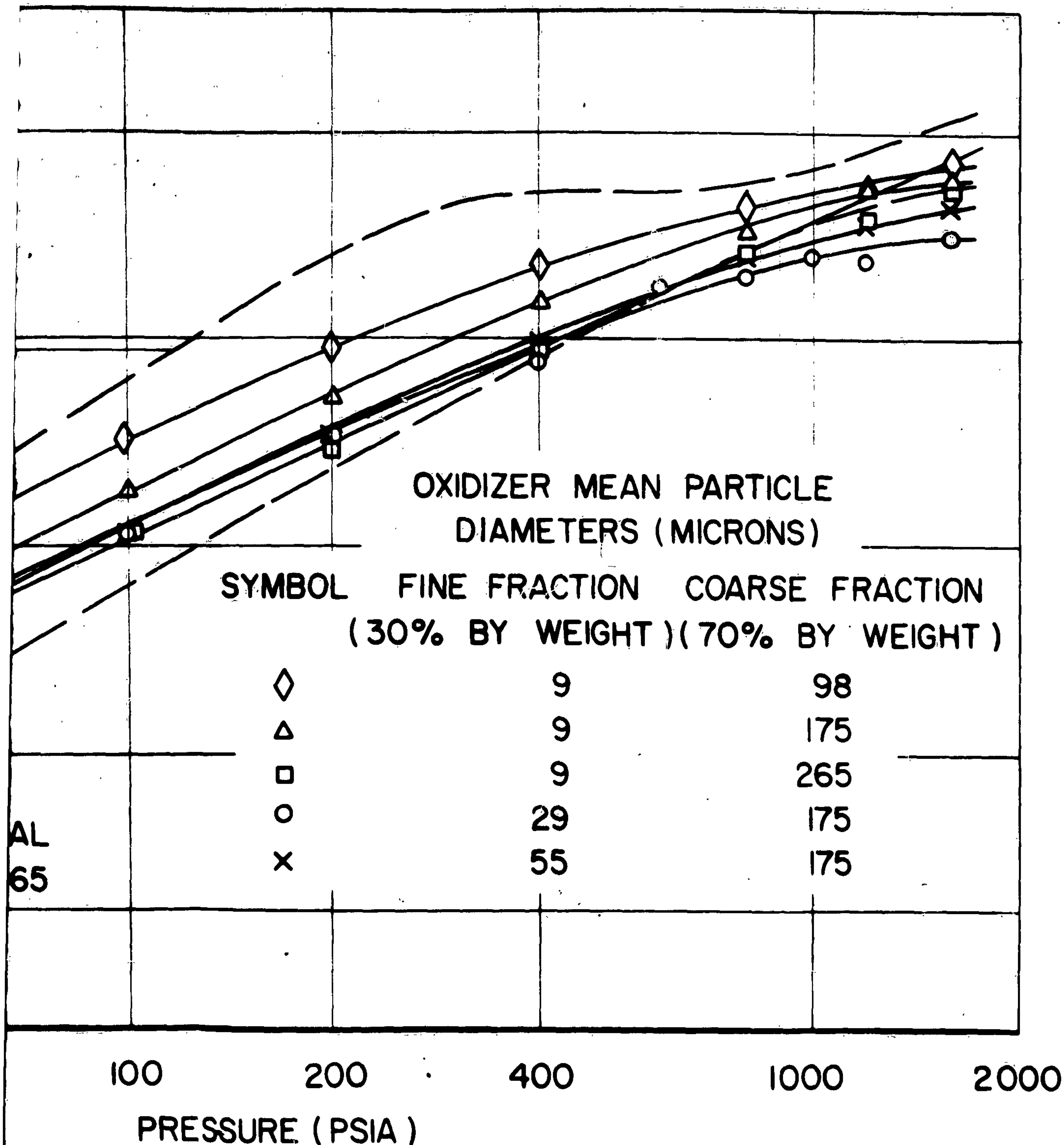

GURE 8 BURNING RATE VS PRESSURE
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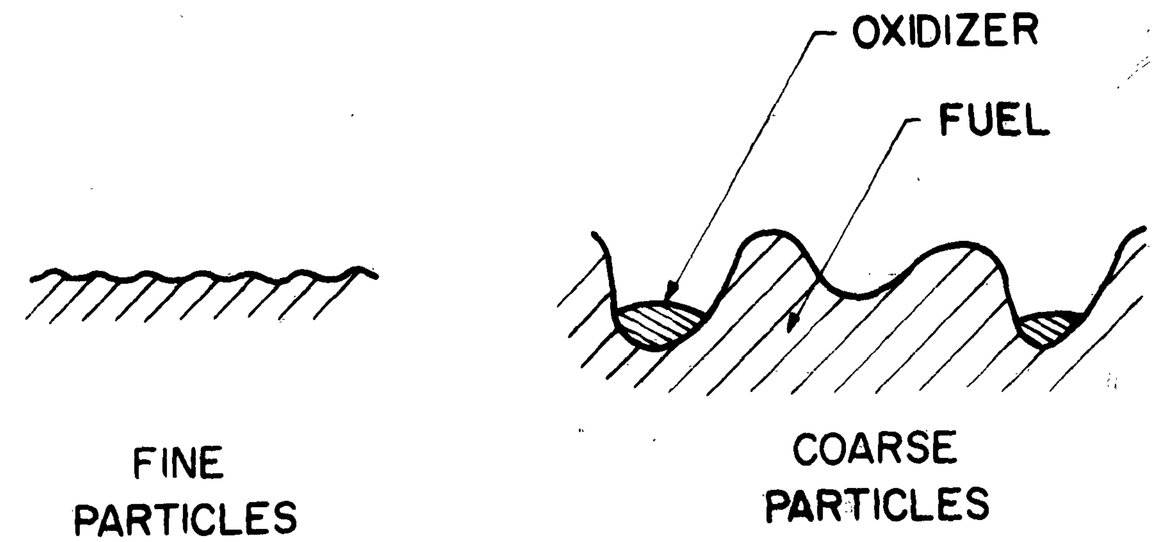
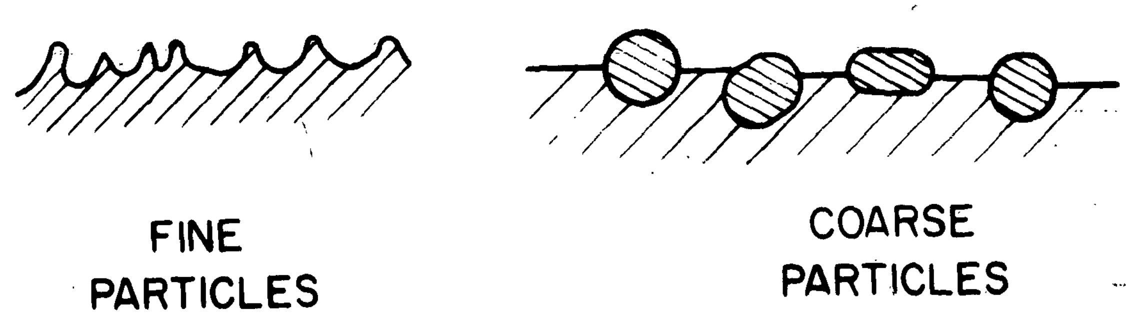


HIGH PRESSURE



LOW PRESSURE

FIGURE 10 PROPELLANT BURNING SURFACES OBTAINED BY VACUUM EXTINGUISHMENT

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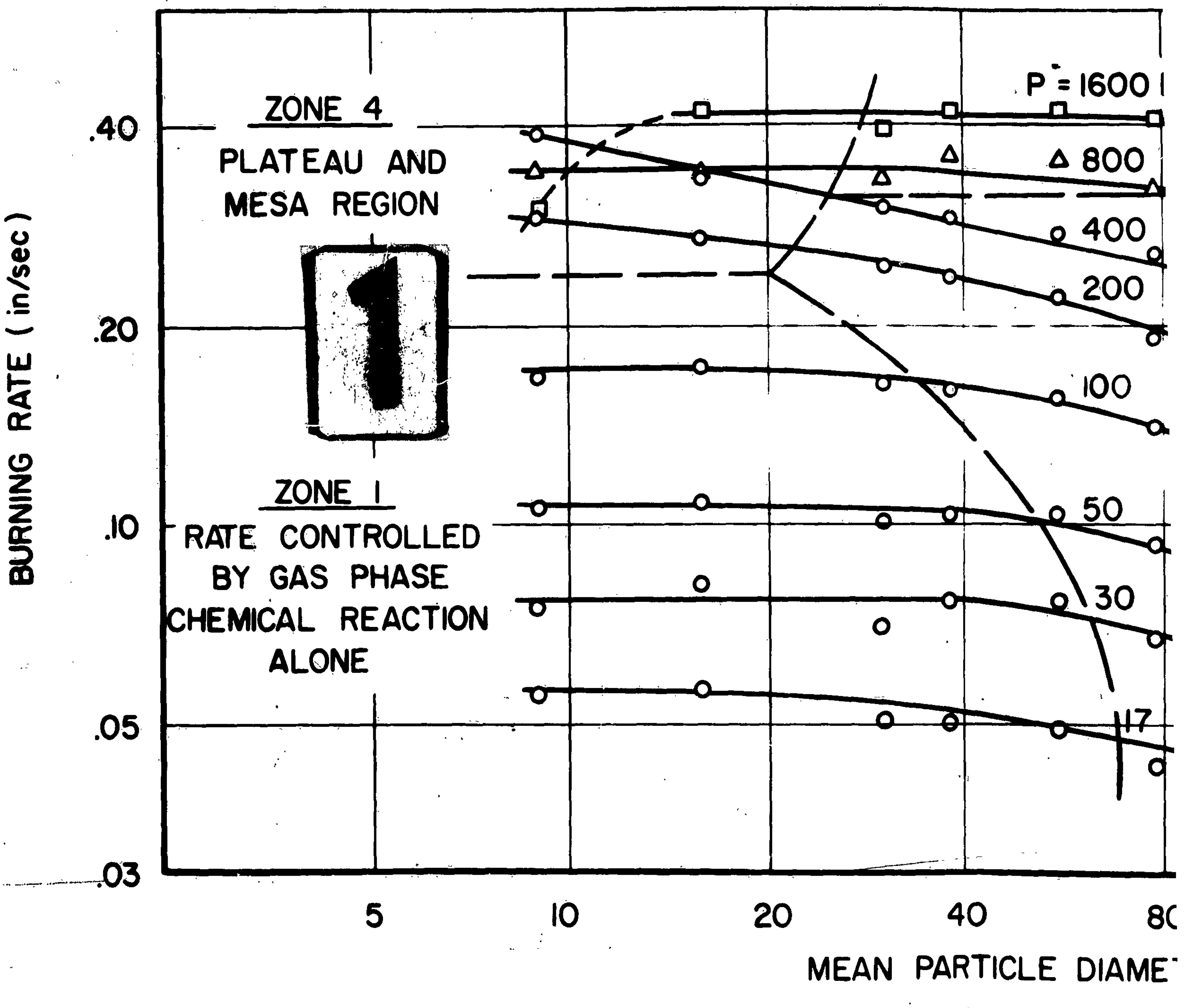
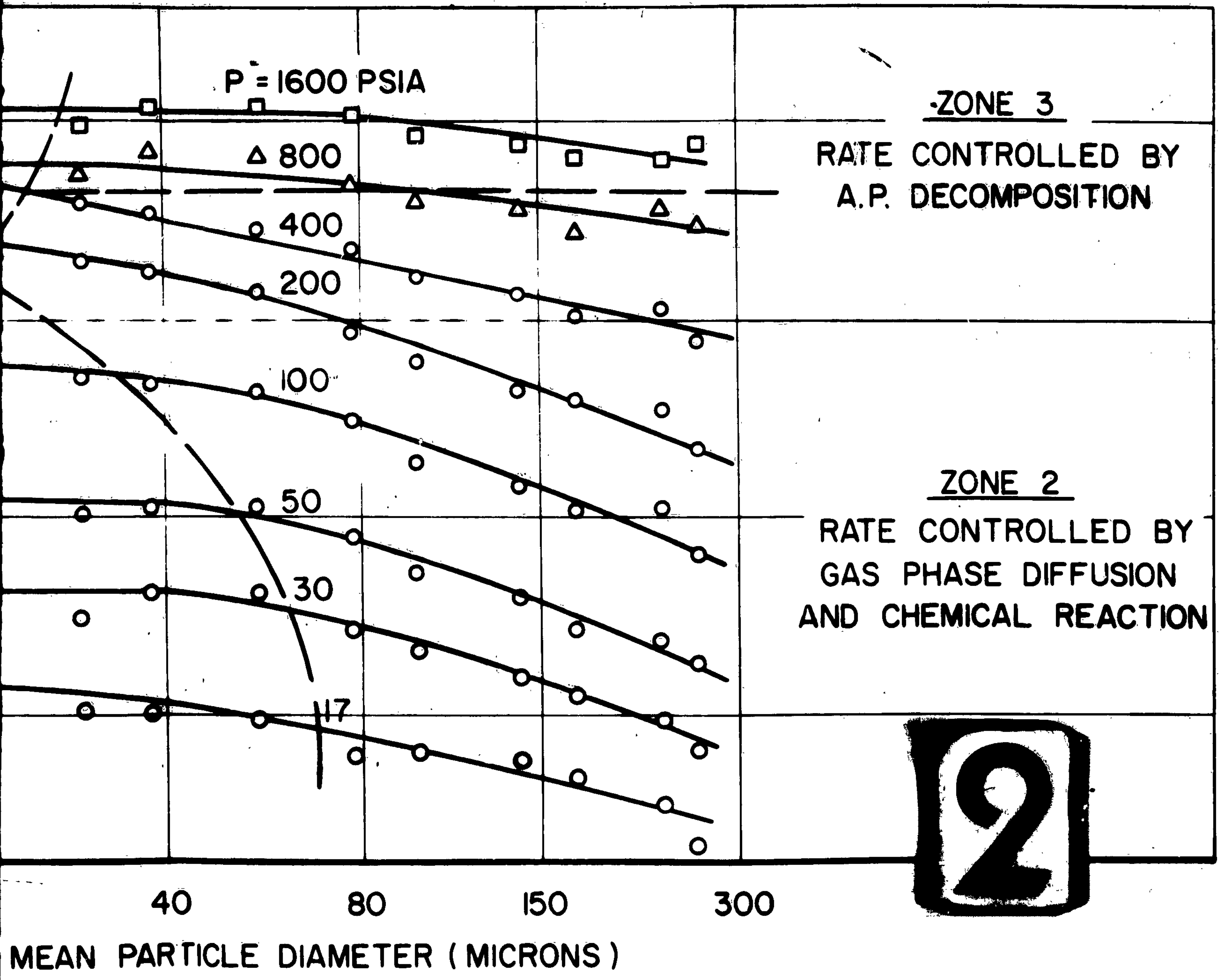


FIGURE 11 DOMAINS OF COMBUSTI
BY BURNING RATE VS PARTICLE
POLYSULFIDE PROPELLANTS, UNIMODAL F



DOMAINS OF COMBUSTION BEHAVIOR INDICATED
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